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(54) Silver halide photographic emulsions utilizing low-dye sensitizations with incorporated fog suppressants

Photographische Silberhalogenidemulsionen mit geringen Farbstoffsensibilisierungen und mit zugesetzten, Schleier unterdrückenden Mitteln

Emulsions photographiques à l'halogénure d'argent avec sensibilisations basses de colorants et avec moyens antivoile incorporés

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(73) Proprietor: **EASTMAN KODAK COMPANY**
Rochester, New York 14650-2201 (US)

(72) Inventors:
- **Irving, Mark Edward, c/o Eastman Kodak Comp.**
  Rochester, New York 14650-2201 (US)
- **Rieger, John Brian, c/o Eastman Kodak Comp.**
  Rochester, New York 14650-2201 (US)
- **Eikenberry, John Nathan,**
  c/o Eastman Kodak Comp.
  Rochester, New York 14650-2201 (US)

(74) Representative: **Brandes, Jürgen, Dr. et al**
Wuesthoff & Wuesthoff
Patent- und Rechtsanwälte
Schweigerstrasse 2
81541 München (DE)

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Description

Technical Field

This invention relates to silver halide photographic materials which are less susceptible to pressure fog, and methods of making same.

Prior Art

Pressure applied to silver halide photographic emulsion coatings can produce both reversible and irreversible effects on the sensitometry of the photographic product. In general, pressure sensitivity can be described as an effect which causes the photographic sensitometry of film products to change after the application of some kind of a mechanical stress to a coated photographic film. The prior art, such as described in James, The Theory of the Photographic Process, 4th Ed., MacMillan (1977), describe various mechanisms in association with the various types of pressure sensitivities observed with photographic products, characterized in that the transmission of mechanical and thermal stress to silver halide crystals causes a change in sensitometry for the photographic products.

Pressure sensitivity may manifest itself in photographic products in the form of pressure fog, resulting in increased density marks after development. Pressure fog, which is often called photoabrasion, is an increasingly large impediment to the manufacture and use of photographic recording materials. The problem can arise from large local stresses applied to the recording materials when small particles of dirt or other irregularities on transport mechanism rollers are pressed against the materials in cameras or other exposing devices or possibly during processing operations. Pressure fog can also result from internal stresses created from gelatin drydown during film manufacture.

Attempts to control this problem have typically included the use of gelatin overcoat layers or plasticizers in the photographic element. However, plasticizers reduce the mechanical strength of the silver halide photographic emulsion layers containing them. Gelatin overcoat layers do not themselves offer adequate protection, because dry gelatin is hard and transmits stress.

US-A-4,925,783 and US-A-4,996,140 describe a method of improving sensitizing dye absorption and pressure blackening performance by adding a sensitizing dye during desalting. US-A-4,659,654 describes a photographic material with reduced pressure blackening which has silver halide particles with a specific iodide composition and containing certain cyanine dyes. These patents provide a very wide range for the amount of sensitizing dye which may be added and they do not indicate any correlation between the amount of sensitizing dye added and the reduction of pressure fog. Sensitizing dyes are typically added at a level which will yield optimum emulsion performance in terms of various parameters including speed, fog, and gamma. The preferred concentration of sensitizing dye is usually from 80% to 100% saturation coverage.

It is known in the art to add various compounds to photographic emulsions to control chemically originated fog. Commonly used antifoggants include various tetraazaindenes and mercaptotetrazoles as disclosed in Research Disclosure, No. 308119, p. 993, (December 1989). Normally such antifoggants are used as melt additives, that is they are added to the emulsion after chemical sensitization and just prior to coating. However, US-A-3,732,104 indicates that tetraazaindenes may be added at any time during emulsion preparation, but preferably just before coating. US-A-4,863,844 relates to a more heat stable photographic element characterized in that certain mercaptotetrazoles are added after the formation of silver halide grains up to the completion of chemical sensitization. US-A-3,637,393 relates to a photographic material with reduced fog which contains certain mercaptotetrazoles and states that it is preferable to add the mercaptotetrazoles during sensitization or prior to coating. US-A-4,912,026 relates to a light-sensitive material with BF contamination resistance and pH variation resistance which contains certain mercaptotetrazoles and states that it is preferable to add the mercaptotetrazoles during sensitization or prior to coating. All of these references are directed toward the reduction of fog created by chemical processes. None of these references are directed to the elimination of pressure fog through the combination of the above antifoggants with reduced sensitizing dye levels.

It has now been found that pressure fog can be reduced in a spectrally sensitized photographic emulsion without a significant loss in speed or upper scale gamma, by adding the sensitizing dye at a concentration of less than 75% of its saturation coverage and adding a heterocyclic antifoggant which contains an acidic sulfur or nitrogen silver binding site to the emulsion during sensitization. It has further been found that such a photographic emulsion also has a good granularity position.

Assessment Of The Art

There is a continuing need in the industry for photographic elements with reduced pressure fog.

Summary Of The Invention

This invention provides a photographic element comprising a support bearing at least one photographic silver halide emulsion layer wherein the photographic silver halide emulsion:

a) contains a spectral sensitizing concentration of at least one spectral sensitizing dye at a concentration of less than 75% of its saturation coverage; and
b) contains an antifogging amount of a heterocyclic antifoggant which contains an acidic sulfur or nitrogen silver binding site.

Further, the photographic silver halide emulsion is prepared by precipitating, spectral/chemical sensitizing and coating the emulsion on the support; and adding the antifoggant prior to or during the spectral/chemical sensitization.

In one embodiment the silver halide emulsion is contained in the silver halide emulsion unit furthest from the support. In another embodiment the silver halide emulsion is a bromoiodide emulsion. In additional embodiments the silver halide emulsion is a tabular emulsion or an octahedral emulsion.

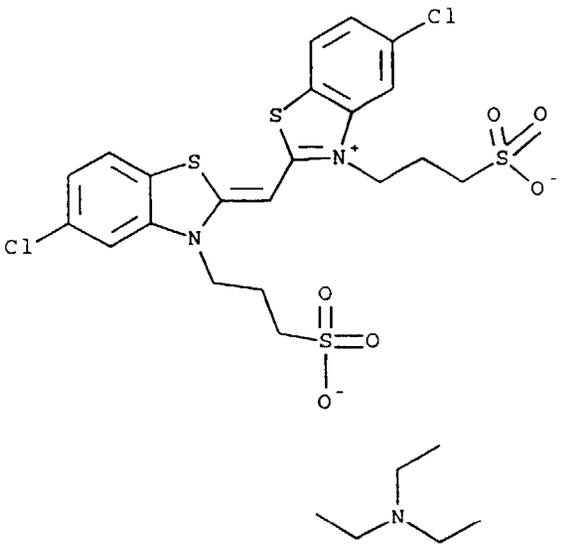
This invention further provides a method of preparing a photographic silver halide emulsion comprising precipitation and spectral/chemical sensitization steps to enable a spectrally sensitized silver halide emulsion containing spectral sensitizing dye at a concentration of less than 75% of its saturation coverage; characterized in that an antifogging amount of a heterocyclic antifoggant which contains an acidic sulfur or nitrogen silver binding site is added prior to or during spectral/chemical sensitization.

Detailed Description The Invention

The photographic elements of this invention contain at least one emulsion which is sensitized with a sensitizing dye at a concentration less than approximately 75% of its saturation coverage. The saturation coverage for any given emulsion substrate and any given sensitizing dye can be determined using the Langmuir Isotherm method as described in James, The Theory of the Photographic Process, pp. 236-239, 4th Edition, (1977, Macmillan Publishing Company, Inc.). The concentration of sensitizing dye must, however, be high enough to adequately sensitize the emulsion. This will vary depending on the emulsion type and can be determined by methods known to those skilled in the art. Generally, the concentration should be at least 10% of the saturation coverage. The preferred concentration of sensitizing dye for this invention is from 25 to 75% of its saturation coverage.

While this invention may be used in any silver halide emulsion containing layer of a multilayer silver halide element the more preferred use is in the unit located toward the front surface of the pack. This is because the silver halide emulsion unit which is furthest from the support is more susceptible to pressure fog because it is most directly impacted by the external pressure causing element. The silver halide emulsion unit furthest from the support may actually be more than one layer with the layers being sensitive to the same given region of the spectrum, that is yellow, green, or red. Each layer may also contain more than one emulsion. The emulsion of this invention may be used in one or more of the layers in the unit or in one or more emulsions in a layer.

In conventional multilayer silver halide photographic elements for camera use the unit furthest from the support is the blue light sensitive unit and therefore the preferred use of this invention is with emulsions appropriate for use in the blue light sensitive unit. These would be emulsions sensitized with blue light absorbing sensitizing dyes, examples of which are discussed in Research Disclosure, Item 308119, p. 993, (December, 1989). The preferred blue-light absorbing sensitizing dyes are thiacyanine dyes. The more preferred blue-light absorbing sensitizing dyes are benzothiazole cyanine dyes. The most preferred dye is



SD-1

Although the preferred use of this invention is in the unit furthest from the support it is also useful in other pressure sensitive layers. All the layers of the photographic element are vulnerable to pressure fog created when the photographic element is dried during manufacturing. Therefore this invention may also be used with red and green light absorbing sensitizing dyes in the magenta and cyan emulsion layers of conventional photographic elements.

Photographic emulsions are generally prepared by precipitating silver halide crystals in a colloidal matrix by methods conventional in the art. The colloid is typically a hydrophilic film forming agent such as gelatin, alginic acid, or derivatives thereof.

The crystals formed in the precipitation step are chemically and spectrally sensitized, as known in the art. Chemical sensitization of the emulsion employs sensitizers such as sulfur-containing compounds, for example, allyl isothiocyanate, sodium thiosulfate and allyl thiourea; reducing agents, for example, polyamines and stannous salts; noble metal compounds, for example, gold, platinum and diethylsenide; and polymeric agents, for example, polyalkylene oxides. A temperature rise is employed to complete chemical sensitization (heat spike). As already described spectral sensitization is effected with agents such as sensitizing dyes. For color emulsions, dyes are added in the spectral sensitization step using any of a multitude of agents described in the art. It is known to add such dyes both before and after the heat spike.

After spectral sensitization, the emulsion is coated on a support. Various coating techniques include dip coating, air knife coating, curtain coating and extrusion coating.

In this invention the sensitizing dye may be added to the emulsion by conventional methods. The dye may be added at any point during the spectral/chemical sensitization process and before or during the heat spike which effects chemical sensitization. Combinations of sensitizing dyes may be used as long as the final concentration meets the requirement of this invention.

The silver halide emulsions of this invention are also treated with an antifoggant. It has been found that in order to retain the desired speed, low fog, high gamma and low granularity the low dye emulsion must have the antifoggant added during the sensitization step. The antifoggants may be added at any point after precipitation and before or during the heat spike used to effect sensitization. This time frame is referred to herein as spectral/chemical sensitization.

The antifoggants of this invention are generally heterocyclic antifoggants which contain an acidic sulfur or nitrogen silver binding site. Certain antifoggants, such as 3-(2-methylsulfamoylethyl)-benzothiazolium tetrafluoroborate which contain such sites do not adequately control fog, while maintaining acceptable speed, in the emulsions of this invention. Generally, antifoggants which must ring-open to achieve their antifogging effect do not work in this invention and are excluded therefrom. Antifoggants which are suitable for this invention include but are not limited to: mercaptoazoles, including mercaptotriazoles, mercaptooxadiazoles, mercaptothiadiazoles, mercaptoimidazoles, mercaptobenzazoles, mercaptotetrazoles, and substituted or non-substituted phenylmercaptotetrazoles; tetrazoles, including substituted phenyl tetrazoles; tetraazaindenes, including unsubstituted tetraazaindenes, 2-alkylthio tetraazaindenes with alkyl chain length from 1-10, thioether substituted tetraazaindenes, carboxylic acid substituted tetraazaindenes and pentaazaindene analogs. The more preferred antifoggants are 5-bromo tetraazaindene and 1-phenyl 5-mercaptotetrazole. Particular antifoggants may be preferred for certain emulsion types, emulsion halide structures, sensitizing dyes, and sensitizing dye levels. Combinations of these antifoggants may also be used.

The amount of antifoggant which needs to be added depends on many factors such as emulsion type, other sen-

sitizers, such as thiocyanate, gold or sulfur containing compounds, emulsion halide structure, and emulsion size. In general 0.1 to 10^5 mg/mol Ag is adequate to produce the desired results. The preferred amount of antifoggant to be added is from 1 to 10^3 mg/mol Ag. This level should be co-optimized with the other sensitizer levels.

The antifoggant may be added in any conventional manner suitable for this purpose. They can be added from solutions or as solids. For example, they can be dissolved in a suitable water miscible solvent and directly added to the silver halide emulsion, or they can be added to the emulsion in the form of a liquid dispersion similar to the technique used with certain couplers.

This invention is useful with those emulsions which are sensitive to pressure fog. The pressure sensitivity can be tested by subjecting portions of a coated sample to a roller apparatus fitted with a sandblasted hardened steel wheel. The magnitude of the pressure effect can be quantified by comparing the Dmin density of an unpressured portion to that of a pressured portion of the same sample. The increase in density of the pressured portion is the pressure fog. The magnitude of the pressure fog will depend on the width, diameter and roughness of the wheel, the pressure applied to the wheel, and the speed at which the wheel is rolled over the sample (with the emulsion layers facing the roughened wheel). A typical configuration would be to apply 289,590 Pa (42 psi) pressure on a 4 mm wide by 30 mm diameter sandblasted steel wheel at a linear speed of 300 mm/second. For such a configuration, emulsions sensitive to pressure fog will generally exhibit a pressure fog density that is greater than 5% of the total possible density (Dmax).

Hexahedral, octahedral, cubic, tabular or potato-like silver halide grains are known to be susceptible to deformation by external forces. While this invention may be used with emulsions of any halide content, this invention has proven particularly useful with emulsions which have high detective quantum efficiency as described in James, The Theory of the Photographic Process, p. 636 (4th Edition, Macmillan Publishing Company, New York, 1977). The preferred emulsions of this invention are those used in camera speed photographic elements. Emulsions other than silver bromoiodide have found only limited use in such elements. Therefore this invention is most useful with iodide containing emulsions, especially with bromoiodide emulsions.

The photographic elements can be single color elements or multicolor elements. Multicolor elements typically contain dye image-forming units sensitive to each of the three primary regions of the visible spectrum. Each unit can be comprised of a single emulsion layer or of multiple emulsion layers sensitive to a given region of the spectrum. The layers of the element, including the layers of the image-forming units, can be arranged in various orders as known in the art. In an alternative format, the emulsions sensitive to each of the three primary regions of the spectrum can be disposed as a single segmented layer, for example, as by the use of microvessels as described in US-A-4,362,806. The element can contain additional layers such as filter layers, interlayers, overcoat layers, subbing layers and the like.

In the following discussion of suitable materials for use in the emulsions and elements of this invention, reference will be made to Research Disclosure, December 1989, Item 308119, published by Kenneth Mason Publications, Ltd., Dudley Annex, 12a North Street, Emsworth, Hampshire P010 7DQ, ENGLAND. This publication will be identified hereafter by the term "Research Disclosure".

The silver halide emulsions employed in the elements of this invention can be either negative-working or positive-working. Examples of suitable emulsions and their preparation are described in Research Disclosure Sections I and II and the publications cited therein. Some of the suitable vehicles for the emulsion layers and other layers of elements of this invention are described in Research Disclosure Section IX and the publications cited therein.

The silver halide emulsions can be chemically and spectrally sensitized in a variety of ways, examples of which are described in Sections III and IV of the Research Disclosure. The elements of the invention can include various couplers including but not limited to those described in Research Disclosure Section VII, paragraphs D, E, F and G and the publications cited therein. These couplers can be incorporated in the elements and emulsions as described in Research Disclosure Section VII, paragraph C and the publications cited therein.

The photographic elements of this invention or individual layers thereof can contain among other things brighteners (Examples in Research Disclosure Section V), antifoggants and stabilizers (Examples in Research Disclosure Section VI), antistain agents and image dye stabilizers (Examples in Research Disclosure Section VII, paragraphs I and J), light absorbing and scattering materials (Examples in Research Disclosure Section VIII), hardeners (Examples in Research Disclosure Section X), plasticizers and lubricants (Examples in Research Disclosure Section XII), antistatic agents (Examples in Research Disclosure Section XIII), matting agents (Examples in Research Disclosure Section XVI) and development modifiers (Examples in Research Disclosure Section XXI).

The photographic elements can be coated on a variety of supports including but not limited to those described in Research Disclosure Section XVII and the references described therein.

Photographic elements can be exposed to actinic radiation, typically in the visible region of the spectrum, to form a latent image as described in Research Disclosure Section XVIII and then processed to form a visible dye image examples of which are described in Research Disclosure Section XIX. Processing to form a visible dye image includes the step of contacting the element with a color developing agent to reduce developable silver halide and oxidize the color developing agent. Oxidized color developing agent in turn reacts with the coupler to yield a dye.

With negative working silver halide, the processing step described above gives a negative image. To obtain a

positive (or reversal) image, this step can be preceded by development with a non-chromogenic developing agent to develop exposed silver halide, but not form dye, and then uniformly fogging the element to render unexposed silver halide developable. Alternatively, a direct positive emulsion can be employed to obtain a positive image.

Development is followed by the conventional steps of bleaching, fixing, or bleach-fixing, to remove silver and silver halide, washing and drying.

The following examples are intended to illustrate, without limiting, this invention.

Examples

The pressure sensitivity of the samples in the following examples were tested by subjecting portions of each sample to 289,590 Pa (42 psi) pressure in a roller apparatus fitted with a sandblasted hardened steel wheel. The indentations and ridges on the sandblasted wheel mimic the effect of dirt particles or other imperfections on, for example, camera transport mechanisms.

Both pressured and unpressured portions of each sample were exposed to white light through a grey wedge chart. These samples were then developed using a color negative process, the Kodak C-41 process, as described in the British Journal of Photography Annual of 1988, pp. 196-198 (Kodak is a trademark of the Eastman Kodak Company, U.S.A.).

The magnitude of the pressure effect was quantified by comparing the blue Dmin density of an unpressured portion of a sample to that of a pressured portion of the same sample. The increase in density observed with the pressured portion of a sample is the pressure-fog. Smaller values of the pressure fog are superior in that they indicate that a particular film composition is less susceptible to forming unsightly marks and blemishes.

Example 1

A 3.3 μm ECD by 0.12 μm thick tabular bromoiodide emulsion was prepared by conventional methods as described in US-A-5,061,616. The emulsion consisted of a uniform 2 mole percent iodide tabular host which accounted for 70% of the total silver. On top of this host was precipitated a thin bromoiodide lamina which was 30 mole percent iodide and amounted to 7% of the total silver. The remainder of the emulsion was a secondary lamina composed of silver bromide. Samples B-1 to B-6 were sensitized with the blue light absorbing sensitizing dye SD-1 and with sulphur and gold in the standard manner. The parameters of the sensitization of Samples B-1 through B-6 are shown in Table 1. Samples B-1 and B-2 contained 1.15 mmol/mol Ag of SD-1, or approximately 86% of saturation coverage. Samples B-3 through B-6 contained 0.80 mmoles/mol Ag, of SD-1 or approximately 60% of the saturation coverage. The two antifoggants 1-(3-acetamidophenyl)-5-mercaptotetrazole (APMT) and 5-bromo tetrazaindene (BrTAI) were added during spectral/chemical sensitization. The sensitizations also included 3-(2-methylsulfamolyehtyl)-benzathiazolium tetrafluoroborate (FM-1) which is an antifoggant requiring a ring opening mechanism in order to activate its acidic sulfur atom. The order of addition was thiocyanate, dye, sulfur, gold, FM-1, antifoggant (if any), and finally the chemical ripening step at elevated temperature.

Table I

Sensitizer Levels For Representative Finishes On Tabular Emulsions of Example 1								
Batch Finish	NaSCN mg/mol	SD-1 mm/ mol	Percent dye saturation	Sulfur mg/mol	Gold III mg/mol	FM-1 mg/ mol	Addenda/ mg/mol	temp/time
B-1 (Control)	20	1.15	86	4.0	2.0	40	-	65/10'
B-2 (Control)	20	1.15	86	4.0	2.0	40	-	65/10'
B-3 (Control)	20	0.80	60	4.0	2.0	90	-	65/10'
B-4 (Invention)	20	0.80	60	4.0	2.0	40	APMT/17	65/25'
B-5 (Invention)	20	0.80	60	8.0	4.0	40	APMT/17	65/28'
B-6 (Invention)	25	0.80	60	6.0	3.0	40	BrTAI/100	65/17'

Table 2 is a summary of the photographic data for samples B-1 through B-6. The comparison of sample B-4 with the high dye check shows that although the gamma is lower, it is an improvement over the sample B-3 finish. The fog level and normalized grain are also better for this sensitization. The pressure fog signal was 0.85 relative to the check position of 1.22. B-5 was very similar to the B-4 finish except that the sulfur and gold levels were doubled. The results show that much of the upper scale was regained at the expense of 0.15 log E loss in speed. The gamma normalized granularity actually improved over the check position, and the pressure fog was lowered to 0.85.

The best low dye sensitization was achieved with B-6. In this case, the curve shape was very similar to the high dye control. Speed, fog, and granularity positions were also maintained or improved. The pressure fog was reduced 25% from 1.22 to 0.95.

In addition to the metrics already discussed, the last column of Table 2 indicates the smooth roller pressure desensitization signal through the single value of SUM2. This is an exposure averaged number and is not significantly different for any of the finishes shown. Pressure desensitization is not a concern with these values. These examples have shown how pressure fog can be improved through the practice of this invention. They also show the importance of co-optimization of the spectral/chemical sensitization with antifoggant, dye, and chemical sensitizer levels.

Table II

Summary of Photographic Data On T-Grains						
Batch Finish	DMIN	Relative Log Sensitivity	Relative Gamma	Relative Granularity	Change in DMIN with 289,590 Pa (42 psi) Rough	SUM2 Smooth
B-1	0.22	251	1.0	check	1.25	28
B-2	0.13	251	1.0	check	1.22	54
B-3	0.25	249	0.78	+2	0.85	31
B-4	0.12	255	0.85	0	0.85	56
B-5	0.12	237	1.15	-2	0.85	38
B-6	0.09	246	1.04	-2	0.95	54

Example 2

An octahedral emulsion 0.65 μm in edge length was prepared by using 3.5% run iodide and a 2.5% concentrated iodide addition at 70% total silver as described in EP-A-432,834, Photographic Silver Bromoiodide Emulsions, Elements and Processes, Chang and others, filed September 13, 1991. Samples B-7 to B-11 were sensitized with the blue light absorbing sensitizing dye SD-1 and with sulphur and gold in the standard manner. The parameters of the sensitization of Samples B-7 through B-11 are shown in Table 3. Sample B-7 contained 0.6 mmol/mol Ag of SD-1, or approximately 78% of saturation coverage. Samples B-8 through B-11 contained 0.40 mmoles/mol Ag, of SD-1 or approximately 52% of the saturation coverage. The antifoggant 1-phenyl 5-mercaptotetrazole (PMT)was added during spectral/chemical sensitization. The sensitizations also included 3-(2-methylsulfamolyehtyl)-benzathiazolium tetrafluoroborate (FM-1). The chemicals are listed below in the order of addition.

Table III

Sensitizer Levels For Finishes on Octahedral Emulsions of Example 2							
	Feature	NaSCN mg/mol	DS-1 Saturation Coverage	vAg adj mV	Sulfur/Gold 1 mg/mol	FM-1 mg.mol	PMT mg/mol
B-7	check	100	78%	90	1.52/3.06	30	0
B-8	low dye	100	52%	90	1.52/3.06	30	0
B-9	+10% S/Au	100	52%	90	1.67/3.37	30	0
B-10	+50% mod	100	52%	90	1.67/3.37	45	0
B-11	PMT	100	52%	90	1.67/3.37	30	16.9

Addition Order	Chemical	Source
1	Thiocyanate	sodium thiocyanate
2	Sulfur	sodium thiosulfate pentahydrate
3	Gold I	aurous dithiosulfate dihydrate
4	FM-1	3-(2--methylsulfamoylethyl)-benzothiazolium tetrafluoroborate
5	PMT	1-phenyl 5-mercaptotetrazole

The 10% variation in sulfur/gold level had minimal impact on the emulsion finish. As with the T-grain, the fog could be controlled to some extent with higher levels of FM-1, but unacceptable speed loss was still observed. Adding 16.9 mg PMT/mol to the finish reduced fog and retained the speed/granularity of the high dye finish. Pressure fog of this new finish was reduced from 0.8 delta density 289,590 Pa ((42 psi) rough roller) to 0.35 delta density.

A summary of the photographic data is presented in Table IV. Granularity is expressed in terms of NEQ, which measures noise from granularity readings and integrates them across the useful exposure range. Relative log sensitivity + NEQ is a speed/granularity number which weighs speed and NEQ granularity equally.

	Feature	0-4 DMIN	Relative Log Sensitivity	Relative Gamma	Delta NEQ	Delta Relative Log Sensitivity + NEQ	DMIN with 42 psi 289,590 Pa Rough
B-7	78% Saturation Coverage	0.15	289	1.362	0.00	0.00	0.81
B-8	52% Saturation Coverage	0.20	286	1.437	-0.04	-0.07	0.46
B-9	52% Saturation Coverage	0.20	281	1.452	-0.04	-0.12	0.40
B-10	52% Saturation Coverage	0.20	273	1.424	-0.02	-0.18	0.31
B-11	52% Saturation Coverage	0.19	289	1.414	-0.02	-0.02	0.35

Example 3

The emulsion of Example 2, sensitized and containing PMT as in Sample B-11, was coated in the Least Blue Sensitive Layer (Layer 10) of the photographic film of this example. A three color photographic film was prepared as follows using conventional surfactants, antifoggants and the materials indicated. After providing a developable image and then processing in accordance with the Kodak C-41 process (British Journal of Photographic, pp. 196-198 (1988)) excellent results for example improved color, sharpness, granularity and neutral scale, were obtained. All silver halide emulsions were stabilized with 1.75 g 4-hydroxy-6-methyl-1,3,3a,7-tetraazaindene per mole of silver added prior to coating. All silver halide emulsions were sensitized with the appropriate spectral red, green and blue sensitizing dyes.

Support	mg/m^2	mg/ft^2	
Layer 1			
Antihalation Layer	215	20	Black colloidal silver
	91	8.5	UV absorbing dye coupler (1)
	91	8.5	UV absorbing dye coupler (2)
	14.3	13	Blue filter dye (11)

(continued)

Support	mg/m^2	mg/ft^2	
Layer 1			
	2422	225	Gelatin
Layer 2			
Interlayer	54	5.0	D-Ox scavenging coupler (3)
	861	80.0	Gelatin
Layer 3			
Least Red Sensitive Layer	915	85	Red sensitized silver iodobromide emulsion (4.5% iodide, tabular grains with average grain diameter 1.1 μm and average grain thickness 0.1 μm),
	1238	115	red sensitized silver iodobromide emulsion (0.5% iodide, cubic grains with average edge length 0.21 μm)
	603	56	Cyan dye forming image coupler (4)
	36	3.3	Cyan dye-forming development inhibitor release (DIR) coupler (5)
	86	8.0	Yellow dye-forming image coupler (6)
	3078	286	Gelatin
Layer 4			
Most Red-Sensitive Layer	1291	120	Red sensitized silver iodobromide emulsion (3% iodide, octahedral grains with average grain diameter 0.90 μm)
	54	5.0	Cyan dye-forming image coupler (4)
	32.3	3	Cyan dye-forming masking coupler (7)
	50	4.6	Cyan dye-forming DIR coupler (9)
	11	1.0	Yellow dye-forming image coupler (6)
	2368	220	Gelatin
	4.3	0.4	Cyan dye-forming DIR coupler (8)
Layer 5			
Interlayer	129	12	Oxidized development scavenger coupler (3)
	861	80	Gelatin
	11	1	Green filter dye (10)
	49	4	Blue filter dye (11)
Layer 6			
Least Green-Sensitive Layer	124	15	Green sensitized silver iodobromide emulsion (3% iodide, tabular grains with average grain diameter 0.8 μm, and average grain thickness 0.1 μm)
	592	55.0	Green sensitized silver iodobromide emulsion (0.5% iodide, tabular gains with average grain diameter 0.5 and average grain thickness 0.1 μm)
	161	15.0	Magenta dye-forming image coupler that releases a bleach accelerating fragment (12)
	12	1.1	Magenta dye-forming DIR coupler (13)
	1507	140	Gelatin

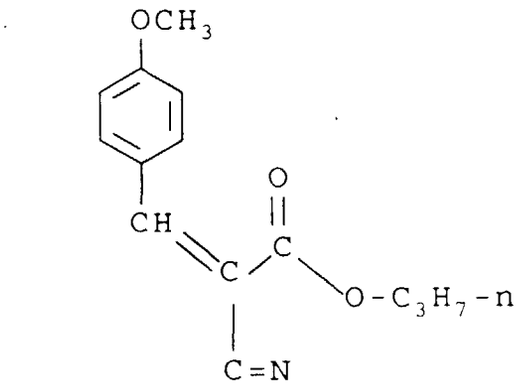
(continued)

Support	mg/m^2	mg/ft^2	
Layer 7			
Mid Green-Sensitive Layer	969	90.0	Green sensitized silver iodobromide emulsion (3% iodide, tabular grains with average grain diameter 0.8 micron and average grain thickness 0.1 μm)
	75.0	7.0	Magenta dye-forming image coupler (14)
	54.0	5.0	Magenta dye-forming image coupler (15)
	9.0	0.8	Magenta dye-forming DIR coupler (13)
	11.0	1.0	Cyan dye forming, image coupler (4)
	1238	115.0	Gelatin
Layer 8			
Most Green-Sensitive Layer	753.0	70.0	Green sensitized silver iodobromide emulsion (6% iodide, tabular grains with average grain diameter 1.0 μm and average grain thickness 0.1 μm)
	22.0	2.0	Magenta dye-forming image coupler (15)
	13.0	1.2	Magenta dye-forming DIR coupler (13)
	65.0	6.0	Magenta dye-forming development masking coupler (16)
	26.0	2.4	Yellow dye-forming DIR coupler (17)
	969	90.0	Gelatin
Layer 9			
Interlayer	75.0	7.0	D-Ox scavenging coupler (3)
	194.0	18.0	Developer bleachable yellow filter dye (18)
	861.0	80.0	Gelatin
Layer 10			
Least Blue-Sensitive Layer	215.0	20.0	Blue sensitized silver iodobromide emulsion (6% iodide, octahedral grains with average grain diameter of 0.65 μm)
	129.0	12.0	Blue sensitized silver iodobromide emulsion (5% iodide, octahedral grains with average grain diameter of 0.40 μm)
	258.0	24.0	Blue sensitized silver iodobromide emulsion (5% iodide, octahedral grains with average grain diameter of 0.23 μm)
	11.0	97.0	Yellow dye-forming image coupler (19)
	1420	132.0	Gelatin
Layer 11			
Most Blue-Sensitive Layer	377.0	35.0	Blue sensitized silver iodobromide emulsion (6% iodide, octahedral grains with average grain diameter of 1.0 μm)
	11.0	1.0	Yellow dye-forming DIR coupler (17)
	1076	100.0	Gelatin
Layer 12			
First Protective Layer	215.0	20.0	Unsensitized silver bromide Lippman emulsion (0.04 μm)
	108.0	10.0	UV absorbing dye (1)
	129.0	12.0	UV absorbing dye (2)
	753.0	70.0	Tricresyl phosphate
	1345	125.0	Gelatin
	40	0.4	Green absorbing dye (10)

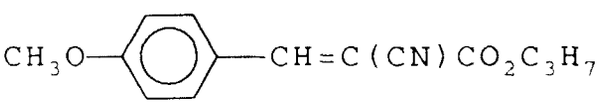
(continued)

Support	mg/m^2	mg/ft^2	
Layer 12			
	20	0.2	Red absorbing dye (20)
Layer 13			
Second Protective Layer	44.0 883.0	4.1 82.0	Matte polyvinyltoluene beads Gelatin

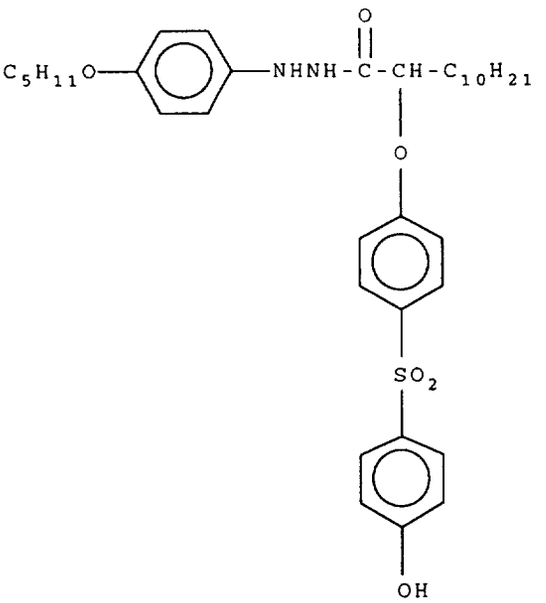
Coupler/Dye Structures



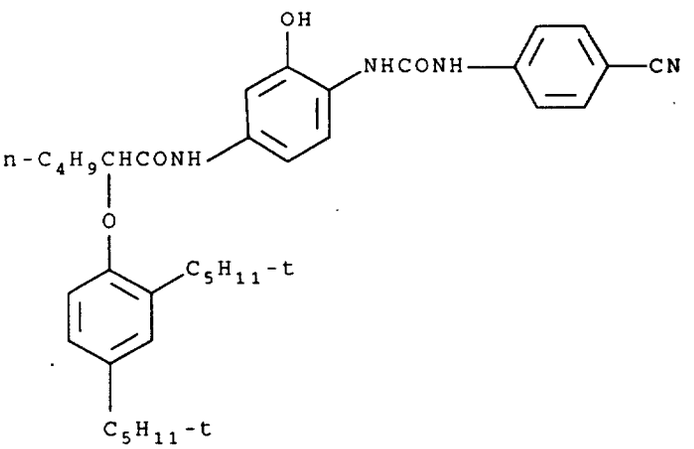
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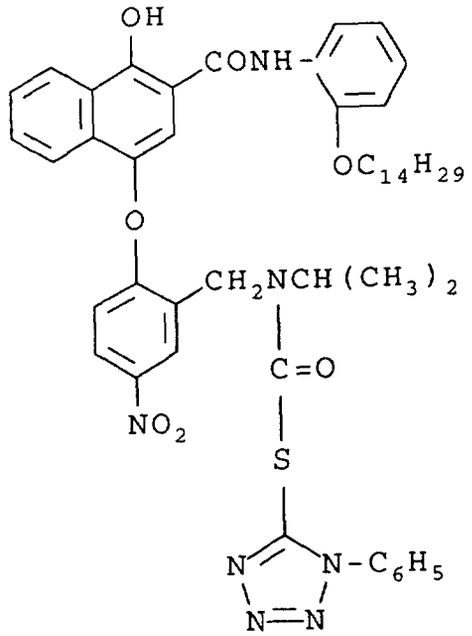
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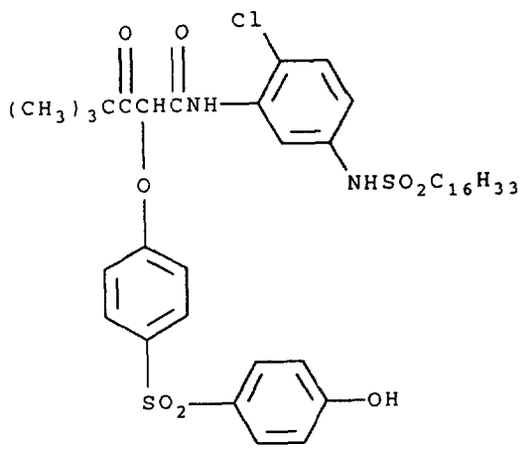
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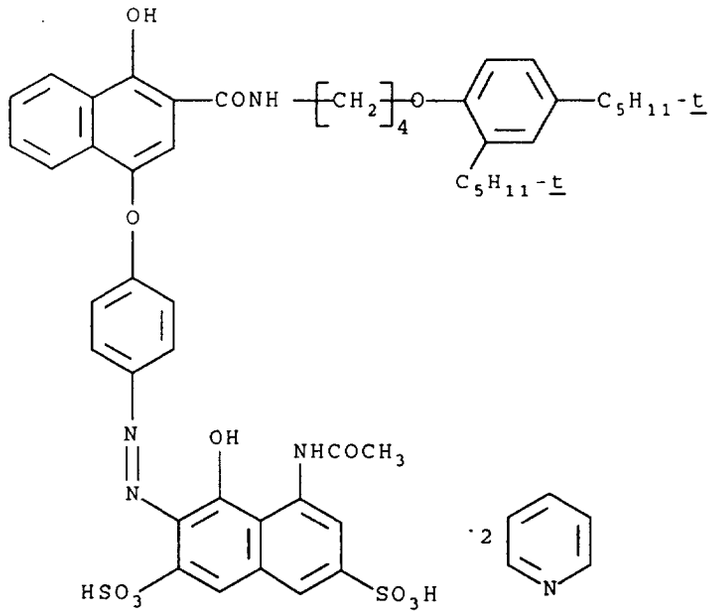
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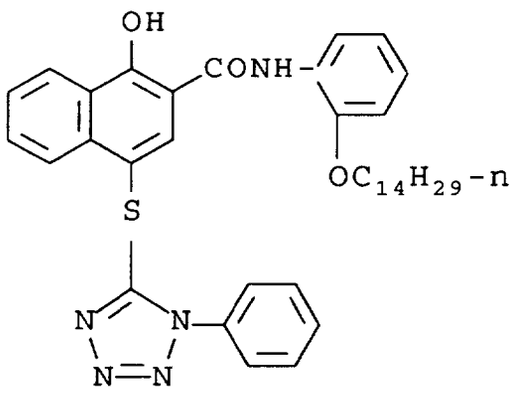
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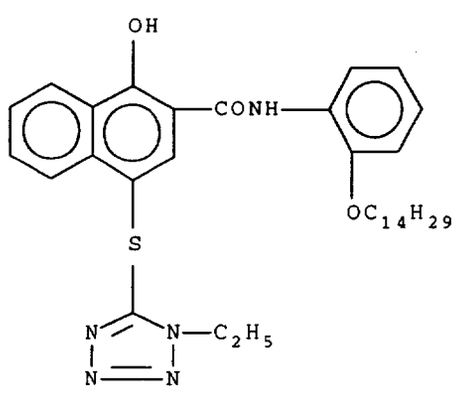
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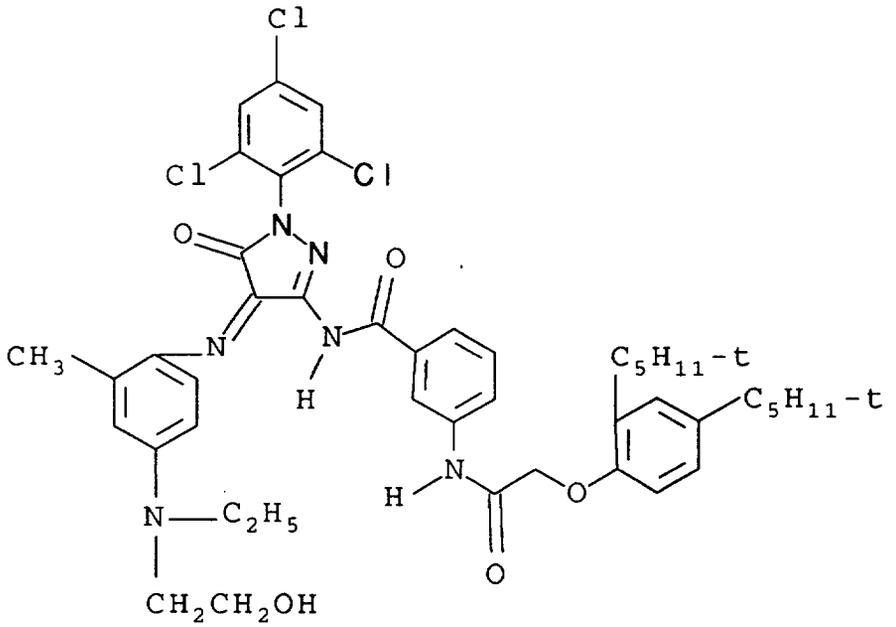
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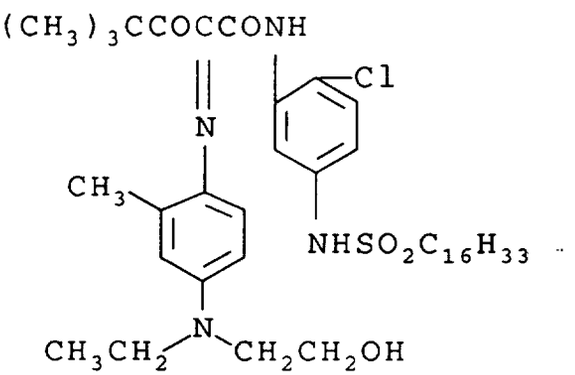
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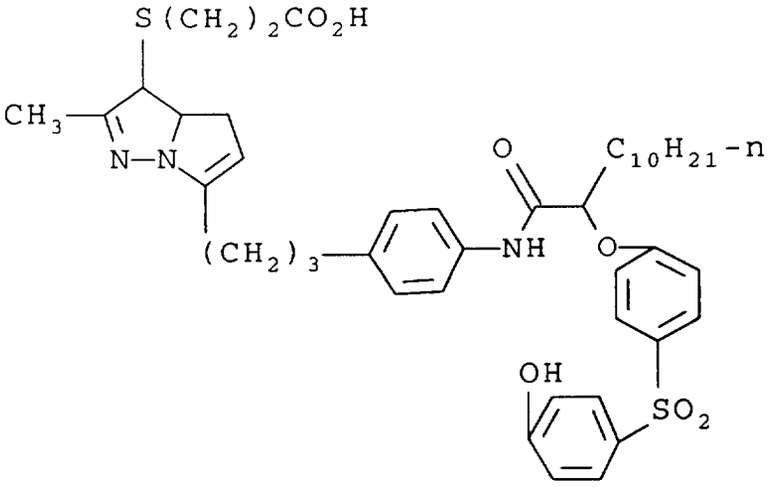
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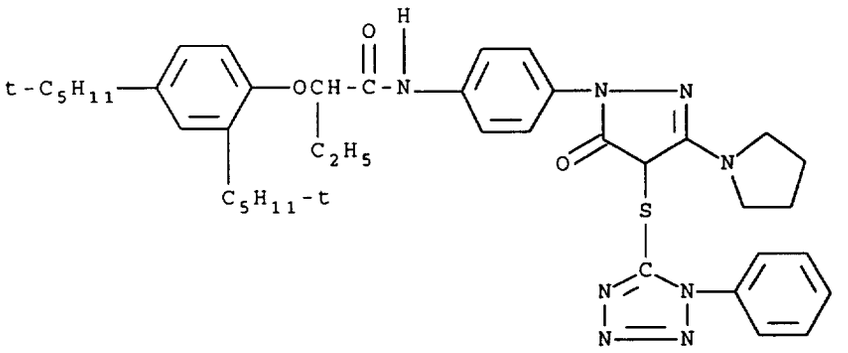
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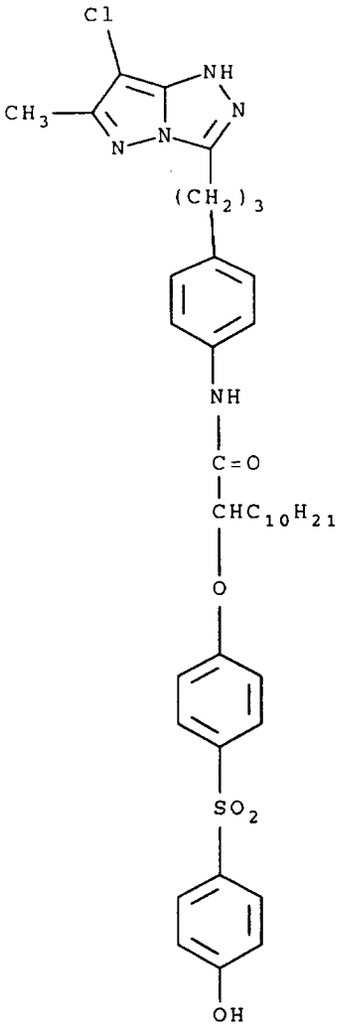
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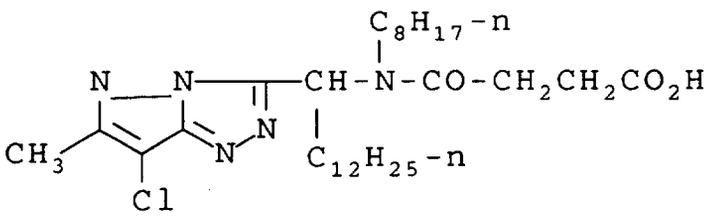
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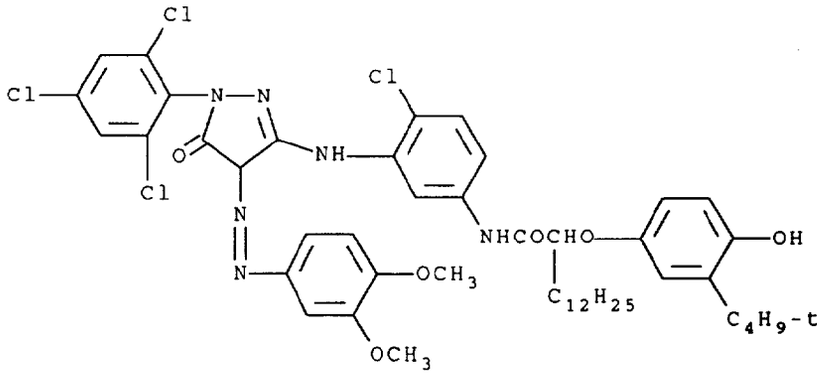
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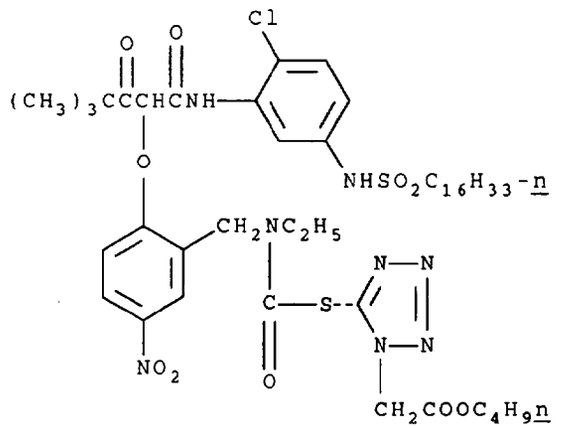
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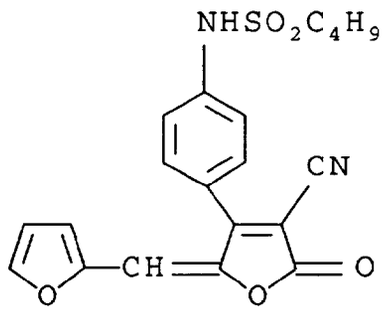
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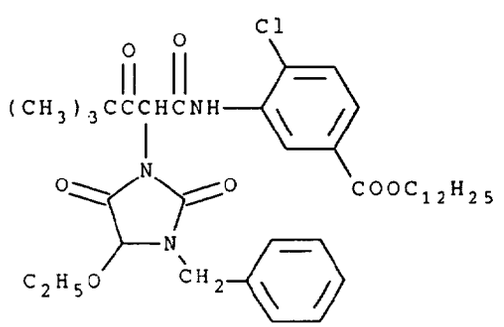
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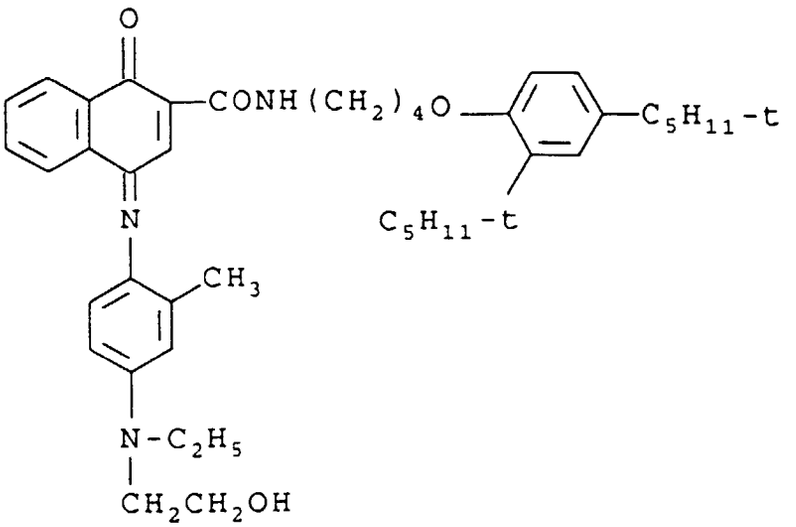
(17)



(18)



(19)



(20)

Claims

1. A photographic element comprising a support bearing at least one photographic silver halide emulsion layer, wherein the photographic silver halide emulsion:

   a) contains a spectral sensitizing concentration of at least one spectral sensitizing dye at a concentration of less than 75% of its saturation coverage:
   b) contains an antifogging amount of a heterocyclic antifoggant which contains an acidic sulfur or nitrogen silver binding site; and
   c) the photographic silver halide emulsion preparation comprised precipitating, spectral/chemical sensitizing and coating the emulsion on the support; and the antifoggant was added prior to or during the spectral/chemical sensitization.

2. The photographic element of claim 1 characterized in that the element contains more than one color unit and characterized in that the silver halide emulsion is contained in the silver halide emulsion color unit furthest from the support.

3. The photographic element of claim 1 or 2 characterized in that the spectral sensitizing dye is a blue light-absorbing sensitizing dye.

4. The photographic element according to any one of the preceding claims characterized in that the silver halide emulsion is a bromoiodide emulsion.

5. The photographic element according to any one of the preceding claims characterized in that the silver halide emulsion is a tabular emulsion.

6. The photographic element according to any one of the preceding claims characterized in that the silver halide emulsion is an octahedral emulsion.

7. The photographic element according to any one of the preceding claims characterized in that the antifoggant is selected from the group consisting of tetraazaindenes or mercaptotetrazoles.

8. The photographic element according to any one of the preceding claims characterized in that the antifogging amount is 0.1 to 10^5 mg/mol Ag.

9. The photographic element of claim 7 characterized in that the antifoggant is 5-bromo tetraazaindene.

10. The photographic element of claim 7 characterized in that the antifoggant is 1-phenyl 5-mercaptotetrazole.

11. The photographic element according to any one of the preceding claims 3 - 10 characterized in that the blue light absorbing sensitizing dye is a thiacyanine dye.

12. A method of preparing a photographic silver halide emulsion as defined in any one of the preceding claims comprising precipitation and spectral/chemical sensitization steps to enable a spectrally sensitized silver halide emulsion, and wherein an antifogging amount of a heterocyclic antifoggant which contains an acidic sulfur or nitrogen silver binding site is added prior to or during spectral/chemical sensitization.

Patentansprüche

1. Photographisches Element mit einem Träger, auf dem sich mindestens eine photographische Silberhalogenidemulsionsschicht befindet, wobei die photographische Silberhalogenidemulsion:

   a) eine spektral sensibilisierende Konzentration von mindestens einem spektral sensibilisierenden Farbstoff in einer Konzentration von weniger als 75 % seiner Sättigungsbeschichtung enthält;

   b) eine eine Antischleierwirkung hervorrufende Menge eines heterocyclischen Antischleiermittels enthält, das eine saure Schwefel- oder Stickstoff-Silberbindungsstelle enthält; und

   c) die Herstellung der photographischen Silberhalogenidemulsion umfaßt die Ausfällung, spektrale/chemische Sensibilisierung und das Auftragen der Emulsion auf den Träger; und wobei das Antischleiermittel vor oder während der spektralen/chemischen Sensibilisierung zugesetzt wurde.

2. Photographisches Element nach Anspruch 1, dadurch gekennzeichnet, daß das Element mehr als eine Farbeinheit aufweist und dadurch gekennzeichnet ist, daß die Silberhalogenidemulsion in der Silberhalogenidemulsions-Farbeinheit enthalten ist, die vom Träger am weitesten entfernt ist.

3. Photographisches Element nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß der spektral sensibilisierende Farbstoff ein blaues Licht absorbierender sensibilisierender Farbstoff ist.

4. Photographisches Element nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Silberhalogenidemulsion eine Bromoiodidemulsion ist.

5. Photographisches Element nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Silberhalogenidemulsion eine Tafelkornemulsion ist.

6. Photographisches Element nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die Silberhalogenidemulsion eine oktaedrische Emulsion ist.

7. Photographisches Element nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das Antischleiermittel ausgewählt ist aus der Gruppe bestehend aus Tetrazaindenen oder Mercaptotetrazolen.

8. Photographisches Element nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß die eine Antischleiermittelwirkung hervorrufende Menge bei 0,1 bis 10^5 mg/Mol Ag liegt.

9. Photographisches Element nach Anspruch 7, dadurch gekennzeichnet, daß das Antischleiermittel 5-Bromo-tetrazainden ist.

10. Photographisches Element nach Anspruch 7, dadurch gekennzeichnet, daß das Antischleiermittel l-Phenyl-5-mercaptotetrazol ist.

11. Photographisches Element nach einem der vorstehenden Ansprüche 3 bis 10, dadurch gekennzeichnet, daß der blaues Licht absorbierende sensibilisierende Farbstoff ein Thiacyaninfarbstoff ist.

12. Verfahren zur Herstellung einer photographischen Silberhalogenidemulsion wie in einem der vorstehenden Ansprüche definiert, das umfaßt die Ausfällung und spektrale/chemische Sensibilisierungsstufen, um eine spektral sensibilisierte Silberhalogenidemulsion zu erzeugen, und bei dem eine eine Antischleiermittelwirkung hervorru-

fende Menge eines heterocyclischen Antischleiermittels, das eine saure Schwefel- oder Stickstoff-Silberbindungsstelle enthält, vor oder während der spektralen/chemischen Sensibilisierung zugesetzt wird.

Revendications

1. Elément photographique comprenant un support recouvert d'au moins une couche d'émulsion photographique aux halogénures d'argent, dans lequel l'émulsion photographique aux halogénures d'argent :

   (a) contient une concentration efficace d'au moins un colorant sensibilisateur spectral à une concentration inférieure à 75 % de son taux de couverture maximal ;
   (b) contient une quantité efficace d'un antivoile hétérocyclique contenant un site de liaison pour l'argent avec un atome acide de soufre ou d'azote ; et
   (c) la préparation de l'émulsion photographique aux halogénures d'argent comprend la précipitation, la sensibilisation spectrale/chimique et le couchage de l'émulsion sur le support ; et l'antivoile est ajouté avant ou pendant la sensibilisation spectrale/chimique.

2. Elément photographique selon la revendication 1, caractérisé en ce que l'élément photographique contient plusieurs unités chromogènes et caractérisé en ce que l'émulsion aux halogénures d'argent est contenue dans l'unité chromogène la plus éloignée du support.

3. Elément photographique selon la revendication 1 ou 2, caractérisé en ce que le colorant sensibilisateur spectral est un colorant sensibilisateur absorbant la lumière bleue.

4. Elément photographique selon l'une quelconque des revendications précédentes, caractérisé en ce que l'émulsion aux halogénures d'argent est une émulsion au bromoiodure.

5. Elément photographique selon l'une quelconque des revendications précédentes, caractérisé en ce que l'émulsion aux halogénures d'argent est une émulsion à grains tabulaires.

6. Elément photographique selon l'une quelconque des revendications précédentes, caractérisé en ce que l'émulsion aux halogénures d'argent est une émulsion à grains octaédriques.

7. Elément photographique selon l'une quelconque des revendications précédentes, caractérisé en ce que l'antivoile est choisi dans le groupe constitué des tétraazaindènes et des mercaptotétrazoles.

8. Elément photographique selon l'une quelconque des revendications précédentes, caractérisé en ce que la quantité d'antivoile est comprise entre 0,1 et 10^5 mg/mole d'Ag.

9. Elément photographique selon la revendication 7, caractérisé en ce que l'antivoile est le 5-bromotétraazaindène.

10. Elément photographique selon la revendication 7, caractérisé en ce que l'antivoile est le 1-phényl-5-mercaptotétrazole.

11. Elément photographique selon l'une quelconque des revendications 3 à 10 précédentes, caractérisé en ce que le colorant sensibilisateur absorbant la lumière bleue est un colorant thiacyanine.

12. Procédé de préparation d'une émulsion photographique aux halogénures d'argent telle que définie dans l'une quelconque des revendications précédentes, comprenant les étapes de précipitation et de sensibilisation spectrale/chimique pour obtenir une émulsion aux halogénures d'argent sensibilisée spectralement, et dans lequel une quantité efficace d'un antivoile hétérocyclique contenant un site pour une liaison entre un atome acide de soufre ou d'azote et un atome d'argent, est ajoutée avant ou pendant l'étape de sensibilisation spectrale/chimique.